

NEW SEMICONDUCTORS MAY HELP YOU STAY COOL OR POWER YOUR AUTOMOBILE ELECTRONICS

A search for new materials that are suitable for solid state cooling and power generation applications is underway. Semiconductors with the type I clathrate hydrate crystal structure have potential for such applications due to their unusual physical properties. The details of their structures play a key role in determining both electronic and thermal properties. A combination of resonant and high energy x-ray diffraction probed the disorder associated with atoms in the clathrate cavities and demonstrated that, in both $\text{Cs}_8\text{Cd}_4\text{Sn}_{42}$ and $\text{SrGa}_{16}\text{Ge}_{30}$, the elements making up their frameworks are not randomly distributed over the available sites. Careful modification of the observed disorder may provide a future route to enhanced thermoelectric performance.

Cooling and electrical power generation typically make use of mechanical refrigerators and generators. However, their size, reliability, and sometimes the noise associated with them make them impractical for some applications. All solid-state thermoelectric devices fill a niche where portability, long-term reliability, or localized applicability is

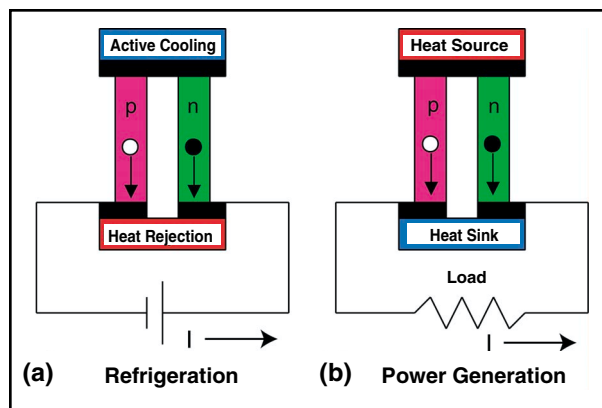


FIG. 1. (a) Simple thermoelectric cooling and (b) power devices make use of both p- and n-type semiconductors. The holes (p) and electrons (n) transport heat as they move through the semiconductors.

crucial, for example, in cooling individual electronic components or powering the *Casini* probe to Saturn. In a thermoelectric cooler [Fig. 1(a)], heat is pumped from one end of the device to a heat sink using a current passing through pieces of semiconducting material. For a

thermoelectric generator [Fig. 1(b)], the hot source supplies thermal energy for conversion into electrical energy. The efficiency of these devices is determined by the transport properties of the semiconductors. An ideal material should have a low resistance so that resistive heating (I^2R) is minimized. It should have a low thermal conductivity so that very little heat can leak back from the heat sink to the component that is being cooled. Finally, each charge carrier passing through the device should transport with it a large amount of heat (large Peltier and Seebeck coefficients). The current generation of devices makes use of thermoelements that are alloys of Bi_2Te_3 (cooling) or Si with Ge (power generation). While these alloys have been in use for several decades, their efficiency is not high.

A vigorous search for new materials suitable for use in high-efficiency thermoelectric applications began in the 1990s. However, finding materials that meet the sometimes conflicting physical property requirements is challenging. Glen Slack has proposed that the ideal material for thermoelectric applications needs to combine the very low thermal conductivity displayed by glasses with the good charge carrier mobilities typically found in crystalline materials. Such an unusual combination of properties can be realized by preparing crystalline

framework materials with “rattling” atoms held inside cavities in the framework. In ideal cases, the “rattlers” scatter the vibrations (phonons) responsible for heat transport, leading to glass-like thermal conductivity, and the well-ordered framework provides for good charge carrier mobility. Such phonon glass electron crystal (PGEC) materials have been found in families of compounds referred to as clathrates and filled skutterudites. For example, the thermal conductivity of the crystalline type-I clathrate semiconductor $\text{Sr}_8\text{Ga}_{16}\text{Ge}_{30}$ is similar to that of an amorphous material in both its magnitude and temperature dependence. In fact, at room temperature, its thermal conductivity is lower than that of vitreous silica and very close to that of amorphous germanium.

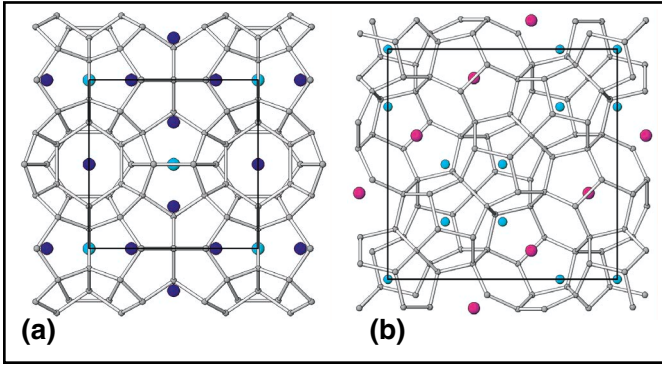


FIG. 2. Semiconductors with clathrate (a) type-I and (b) type-II structures have frameworks built up from covalently bonded atoms such as Ga, Ge, Si, and Sn. Alkali, alkaline earth, or rare-earth atoms occupy cavities in the structure.

Materials with both the type-I and type-II clathrate structures (Fig. 2) have been studied with thermoelectric applications in mind. In some cases, they have also been found to display interesting superconducting and optoelectronic behavior. They are close structural relatives of gas hydrates such as $(\text{Cl}_2)_8(\text{H}_2\text{O})_{46}$ and $(\text{CO}_2)_{24}(\text{H}_2\text{O})_{136}$. Compounds of this type have been known since the early 1800s, and they are currently of great interest as sea floor reservoirs of trapped methane. They have a hydrogen bonded network of water molecules forming a framework around the small gas molecules. In the materials of interest for thermoelectric applications, the framework is built up from elements such as Si, Ge, Sn, and Ga, and the enclathrated “guests” or rattlers are alkali, alkaline earth, or rare-earth,

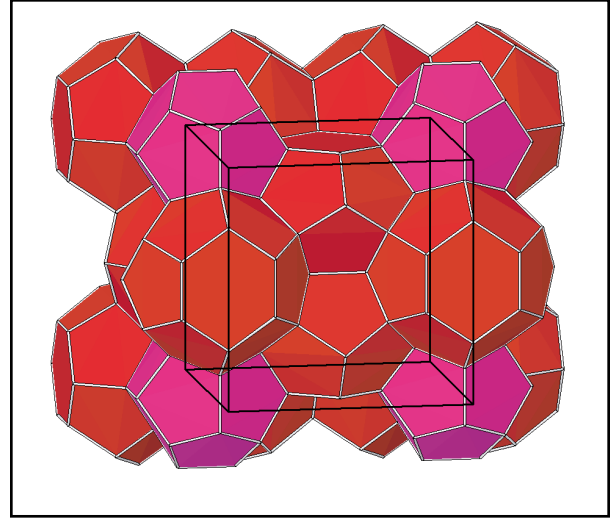


FIG. 3. The type-I clathrate framework is built up from face sharing dodecahedra (pink) and tetrakaidecahedra (red).

metal atoms. It is frequently useful to think of these structures as being constructed from face-sharing polyhedra of different sizes: dodecahedra and tetrakaidecahedra (Fig. 3) for type-I materials, and dodecahedra and hexakaidecahedra for type-II compounds.

The type-I clathrates of interest for thermoelectric applications are Zintl phases. They formally have four valence electrons for every atom in the framework. This leads to stoichiometries such as $\text{Sr}_8\text{Ga}_{16}\text{Ge}_{30}$ and $\text{Rb}_8\text{Ga}_8\text{Ge}_{38}$. In these cases, gallium with three valence electrons per atom replaces some of the germanium atoms to compensate for the valence electrons associated with the strontium or rubidium. Elements, such as gallium, that are introduced to maintain the correct electron count potentially introduce disorder into the framework. On theoretical grounds, the distribution of the substituting elements in the framework is thought to have a dramatic influence on the material’s thermoelectric properties.

We have performed powder x-ray diffraction measurements on clathrates to study the disorder both associated with rattling in the cavities and arising from substitution into the framework. These experiments help us understand both the thermal and electronic properties of the materials.

The use of unusually high-energy x-rays (e.g., ~ 80 keV, corresponding to a wavelength of ~ 0.15 Å),

provides a time-averaged view of the rattling behavior in clathrates such as $\text{Eu}_8\text{Ga}_{16}\text{Ge}_{30}$ and $\text{Cs}_8\text{Na}_{16}\text{Ge}_{136}$ without the absorption problems that often plague powder diffraction at more conventional photon energies. In the case of $\text{Eu}_8\text{Ga}_{16}\text{Ge}_{30}$, these measurements reveal that the europium in the tetrakaidecahedral cavities does not undergo a simple rattling motion about the center of the cavity. The metal is moving in a potential well with multiple minima and can be considered to be spending most of its time displaced toward the cavity walls. Short wavelength x-rays provide a detailed picture of these europium displacements in the cavity. The considerable advantages associated with the use of high-energy x-rays for diffraction experiments can only be properly realized at facilities such as the Advanced Photon Source (APS). Earlier generation machines do not provide the required high brightness beams of high-energy x-rays.

The issue of disorder within the framework is, in some important cases, very difficult to address. In an x-ray diffraction experiment, the ability to distinguish between two different elements typically depends on the number of electrons that each element has. Consequently, it is impossible to distinguish between the different framework elements in materials such as $\text{Cs}_8\text{Cd}_4\text{Sn}_{42}$ and $\text{Sr}_8\text{Ga}_{16}\text{Ge}_{30}$, because the framework components have almost the same number of electrons as one another. However, by using x-rays that have been carefully selected so that their energy is close to that needed to eject an electron from one of the framework elements, it is possible to distinguish between atoms that have almost the same number of electrons as one another. In these resonant diffraction experiments, changes in x-ray energy effectively tune the scattering powers of the elements involved. Once again, the APS offers considerable

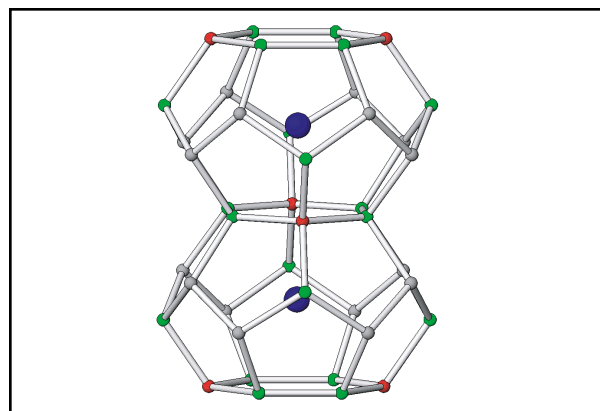


FIG. 4. The different elements in $\text{Sr}_8\text{Ga}_{16}\text{Ge}_{30}$ and $\text{Cs}_8\text{Cd}_4\text{Sn}_{42}$ are not randomly distributed over the three different framework environments (red, green, and grey).

advantages over alternative facilities. The availability of intense beams of high-energy x-rays greatly expands the range of resonant scattering measurements that can be performed. Our work has demonstrated that, in both $\text{Cs}_8\text{Cd}_4\text{Sn}_{42}$ and $\text{Sr}_8\text{Ga}_{16}\text{Ge}_{30}$, the elements making up the framework are not randomly distributed among the three distinct chemical environments in the type-I clathrate framework (Fig. 4). This observation has implications for our understanding of these materials' thermoelectric properties, and it is contrary to the expectations of some workers in the field. Careful modification of this disorder in the framework may provide a future route to enhanced thermoelectric performance.

Principal publication: "Preparation, Transport Properties and Structure Analysis by Resonant X-ray Scattering of the Type-I Clathrate $\text{Cs}_8\text{Cd}_4\text{Sn}_{42}$," A.P. Wilkinson, C. Lind, R.A. Young, S.D. Shastri, P.L. Lee and G.S. Nolas, submitted for publication.

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